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ATMOSPHERIC DEPOSITION OF CHLORINATED COMPOUNDS IN THE GREAT LAKES BASIN.  
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Introduction

Atmospheric deposition is an important pathway by which chlorinated organic compounds enter the Great Lakes. Total polychlorinated biphenyls (PCB) and organochlorine pesticides have been reported in rain and snow samples collected in the Great Lakes basin since the mid-1970s (e.g. Murphy and Rzesutko (1977) and Strachan and Huneault, (1979)). These compounds are ubiquitous and are often detected even in isolated locations. Long range transport has been implicated for the movement and wide distribution of chlorinated organic compounds throughout the Great Lakes basin (Swackhamer *et al.*, 1988).

Chlorinated organic compounds are monitored by the Deposition Monitoring Group of the Air Resources Branch at four rural, shoreline sites around the Great Lakes (Pt. Petre, Port Stanley, Shallow Lake and Turkey Lake), an urban shoreline site near Toronto and inland at Dorset (Figure 1). Dorset is a rural site, with no known local sources of the target compounds. The Dorset site provides a basis upon which background levels and sampling precision may be estimated and serves as a long-range transport receptor site. The Toronto Island site is part of the Remedial Action Plan (RAP) for the Toronto waterfront and is representative of an urban environment. The major objectives of the organic deposition monitoring network are to determine the identity and concentrations of trace organics in air and precipitation and to quantify atmospheric deposition of toxic trace organics to the Great Lakes.

A summary of mid-1988 to mid-1989 concentration data of some chlorinated organic compounds in air and precipitation is presented here. The data reported is more precise than earlier data (e.g. Orr *et al.* 1988) because of increased analytical sensitivity. Greater sensitivity was achieved in part by increasing analyte concentrations in the sample extracts.

Methods

Precipitation inputs of organochlorine pesticides and PCB are collected over 28 days with automated M.I.C. Type B wet only collectors. A gravity-fed XAD-2 resin adsorbent column concentrates non-polar semi-volatile organic compounds *in situ*. A glass-fibre particulate filter is located upstream (Figure 2). Sample volumes are usually greater than 10 litres over 28 days. Sampler efficiency is typically 80-90%. High volume (Hi-vol) air samplers incorporating glass-fibre filters and XAD-2 resin cartridges are used to sample for chlorinated pesticides and PCBs in air (Figure 3). Airflow is controlled at 0.42 m<sup>3</sup>/s. Volumes collected are approximately 2500 m<sup>3</sup> over 4 days. Analysis for total PCB and organochlorine pesticides is based on solvent extraction and evaporation of the extract to increase the analyte concentration factor, florisil column fractionation and dual column high resolution gas chromatography with electron capture detection (HRGC/ECD). The compounds are identified by their retention times and quantitated by measurement of peak areas relative to calibration standards.

Results and Discussion

Summary statistics for precipitation are reported for HCB (Hexachlorobenzene), total PCB (sum of individual congeners) and  $\alpha$ - and  $\gamma$ -BHC (Hexachlorocyclohexane) for the period April 1988 to April 1989 (Table 1). Summary statistics for air are reported from September 1988 to April 1989 (Table 1). All data are reported as concentrations for filter plus cartridge. PCB, HCB, and  $\alpha$ - and  $\gamma$ -BHC are the most commonly detected compounds in precipitation and air. Other species (e.g. DDT group and chlordane) are observed only intermittently and are not reported here. PCB are found in 68% of all precipitation samples analyzed. HCB,  $\alpha$ -BHC and  $\gamma$ -BHC are found in 37%, 39% and 22% of precipitation samples. Reported positives (samples with target compound concentrations greater than minimal detection limits) are much greater in air samples. Percentage of air samples with reported positives ranges from 79.5% for PCB to 75% for  $\gamma$ -BHC. Air data are considerably greater than minimum levels of detection because of the large sample volumes

collected.

Very few positives were reported for precipitation samples collected during 1986 and 1987 (Orr *et al.*, 1988). Using a limited number of samples, volume weighted concentrations were reported by Reid *et al.* (1988) for 1987 data. HCB ranged from 0.03-0.39 ng/l,  $\alpha$ -BHC from 0.37-8.30 ng/l and  $\gamma$ -BHC from 0-2.4 ng/l. Volume weighted mean concentrations for 1988/89 data are comparable to these results (Table 1). The 1988/89 data were obtained using a more sensitive analytical method. Sensitivity was enhanced overall by increasing the analyte concentration factor. Sensitivity for PCB was improved through quantitation of specific congeners. This decreased detection limits by 2 orders of magnitude for PCB but only by a factor of 2 for HCB,  $\alpha$ -BHC and  $\gamma$ -BHC. The relatively low percentage of positives reported in this paper for all of the target compounds except PCB imply that precipitation concentrations for many of the target compounds remain at or below the detection limit.

Within site variability in precipitation concentrations of the target species is generally greater than that between sites (Table 1). It is not known why PCB concentrations in precipitation are much greater at Dorset and Pt. Petre. It is interesting that elevated PCB levels are also reflected in the air samples from these sites. There are no local PCB sources near Dorset or Pt. Petre. HCB,  $\alpha$ - and  $\gamma$ -BHC and PCB concentrations in air are relatively uniform both within and between sites. Air concentrations are comparable to data reported at other continental locations in North America and Europe (e.g. Bidleman *et al.*, 1988 and Atlas and Giam, 1988) and to those reported by Orr *et al.* (1988) for 1987 air samples collected at Dorset and Port Stanley.

#### Conclusions

Preliminary data have been presented from a network operated by the Ontario Ministry of the Environment. There is good general agreement between these results and other findings in the literature. The following areas to improve the monitoring effort have been identified and should be addressed:

#### Recommendations

- 1) The data presented here are preliminary and limited to relatively few sites. No data is available from the western end of Lake Superior or from Lake Michigan. The network needs to be expanded to include more sampling sites to improve representativeness and properly characterize Great Lakes deposition. At least 2 sites should also be collocated as a quality control.
- 2) Data are available for only a single year. Data must be collected over a period of several years to characterize long term atmospheric inputs and identify processes and seasonal variability in deposition.
- 3) Sampling methods need to be extended to distinguish between organic inputs in rain, snow, particle deposition and vapour exchange. In particular methods need to be developed to quantify dry deposition. Dry deposition is very difficult to quantify because of the inadequate size of the data set and large uncertainty in estimating deposition velocities.
- 4) Analytical sensitivity is inadequate to quantify many chlorinated organic species in precipitation. Methods to improve sensitivity (i.e. alternative analytical methods or by increasing sample volume) need to be investigated.
- 4) Because of the expense in operating a sampling network for chlorinated organics or other compounds it is essential that there be close coordination between different monitoring groups to avoid duplication of effort and to enhance information exchange.
- 5) A quality assurance program needs to be incorporated into the monitoring effort to ensure that the data quality characteristics of accuracy, precision, completeness, representativeness and comparability are attained.

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FIGURE 1: MONITORING SITE LOCATION MAP

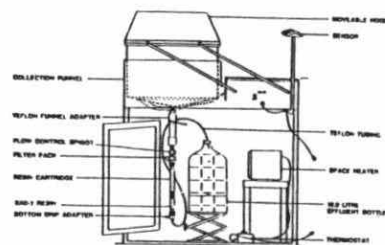


FIGURE 2: MIC 8 PRECIPITATION SAMPLER

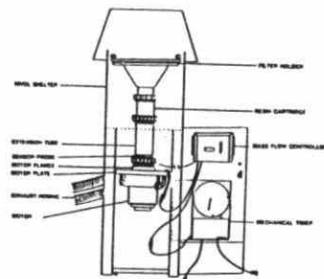


FIGURE 3: 10VOL AIR SAMPLER

TABLE 1: SUMMARY STATISTICS OF SELECTED CHLORINATED ORGANIC COMPOUNDS IN PRECIPITATION AND AIR. LIMITS OF DETECTION (LOD) IN PRECIPITATION (10 LITRES) ARE 0.05 NG/L FOR HCB,  $\alpha$ -BHC AND  $\gamma$ -BHC AND 0.02 NG/L FOR PCB. LOD IN AIR (2500 M<sup>3</sup>) ARE 0.001 NG/M<sup>3</sup> FOR HCB,  $\alpha$ -BHC AND  $\gamma$ -BHC AND 0.0004 NG/L FOR PCB.

SPECIES	PRECIPITATION (NG/L)				AIR (NG/M <sup>3</sup> )			
	HCB	PCB	$\alpha$ -BHC	$\gamma$ -BHC	HCB	PCB	$\alpha$ -BHC	$\gamma$ -BHC
<b>PORT STANLEY</b>								
	N=12 <sup>1</sup>				N=16			
ARITH. MEAN	0.10	10.78	0.91	0.52	0.05	0.28	0.21	0.03
MINIMUM	0.00	00.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.90	43.10	4.00	4.00	0.19	0.77	1.14	0.17
1QUARTILE	0.00	00.00	0.00	0.00	0.01	0.05	0.06	0.01
3QUARTILE	0.04	14.85	1.85	0.25	0.07	0.41	0.25	0.04
VWMEAN <sup>2</sup>	0.09	11.62	0.97	0.24				
<b>DORSET</b>								
	N=11				N=14			
ARITH. MEAN	0.11	74.86	0.38	0.14	0.07	0.41	0.04	0.01
MINIMUM	0.00	2.30	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.40	298.40	2.20	1.00	0.34	3.43	0.16	0.05
1QUARTILE	0.00	22.00	0.00	0.00	0.02	0.07	0.00	0.00
3QUARTILE	0.20	113.50	0.40	0.20	0.07	0.34	0.08	0.02
VWMEAN	0.13	81.79	0.36	0.12				
<b>SHALLOW LAKE</b>								
	N=12				N=10			
ARITH. MEAN	0.06	7.52	2.30	0.61	0.03	0.19	0.10	0.01
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.40	46.00	17.80	4.70	0.08	0.46	0.33	0.04
1QUARTILE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3QUARTILE	0.05	8.10	1.10	0.65	0.06	0.40	0.17	0.03
VWMEAN	0.07	8.12	0.96	0.26				
<b>TURKEY LAKE</b>								
	N=12				N=16			
ARITH. MEAN	0.12	21.70	1.65	0.33	0.05	0.18	0.13	0.02
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.80	105.00	8.30	3.10	0.12	0.66	0.31	0.03
1QUARTILE	0.00	0.00	0.00	0.00	0.01	0.02	0.05	0.01
3QUARTILE	0.16	18.25	2.50	0.00	0.07	0.37	0.20	0.02
VWMEAN	0.11	21.49	1.18	0.27				
<b>PT PETRE</b>								
	N=12				N=11			
ARITH. MEAN	0.72	78.49	0.10	0.00	0.07	0.39	0.17	0.02
MINIMUM	0.00	13.81	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	3.30	179.20	0.60	0.00	0.15	1.01	0.52	0.07
1QUARTILE	0.20	35.90	0.00	0.00	0.04	0.03	0.07	0.00
3QUARTILE	0.42	100.70	0.00	0.00	0.11	0.64	0.22	0.03
VWMEAN	0.37	57.43	0.23	0.00				
<b>TORONTO ISLAND</b>								
	N=12				N=16			
ARITH. MEAN	0.02	25.26	0.92	0.26	0.07	0.40	0.10	0.02
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.20	111.20	7.40	2.70	0.30	2.33	0.32	0.08
1QUARTILE	0.00	0.00	0.00	0.00	0.02	0.11	0.03	0.00
3QUARTILE	0.00	43.90	0.30	0.00	0.10	0.41	0.13	0.03
VWMEAN	0.04	16.08	0.63	0.17				

<sup>1</sup>N EQUALS THE NUMBER OF SAMPLES

<sup>2</sup>VOLUME WEIGHTED MEAN



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